

Quantum-mechanical calculations of the stabilities of fluxional isomers of $C_4H_7^+$ in solution

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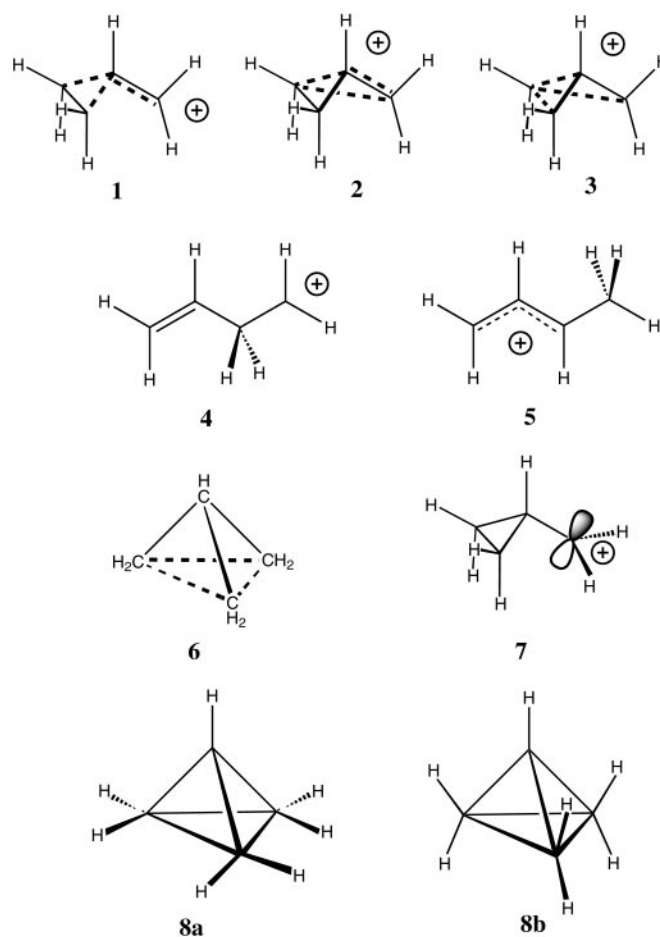
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Although numerous quantum calculations have been made over the years of the stabilities of the fluxional isomers of $C_4H_7^+$, none have been reported for other than the gas phase (which is unrealistic for these ionic species) that exhibit exceptional fluxional properties in solution. To be sure, quantum-mechanical calculations for solutions are subject to substantial uncertainties, but nonetheless it is important to see whether the trends seen for the gas-phase $C_4H_7^+$ species are also found in calculations for polar solutions. Of the $C_4H_7^+$ species, commonly designated bisected-cyclopropylcarbiny 1, *unsym*-bicyclobutonium 2, *sym*-bicyclobutonium 3, allylcarbiny 4, and pyramidal structure 6, the most advanced gas-phase calculations available thus far suggest that the order of stability is $1 \geq 2 \geq 3 \gg 4 \gg 6$ with barriers of only ≈ 1 kcal/mol for interconversions among 1, 2, and 3. We report here that, when account is taken of solvation, 2 turns out to be slightly more stable than 1 or 3 in polar solvents. The pattern of the overall results is unexpected, in that despite substantial differences in structures and charge distributions between the primary players in the $C_4H_7^+$ equilibria and the large differences in solvation energies calculated for the solvents considered, the differential solvent effects from species to species are rather small.

It has been recognized for almost a century that conventional bond formulas with single, double, and triple bonds are not adequate to account for the geometries and reactions of many substances. Elucidation of the structure of diborane was a special watershed, but many earlier ideas such as Thiele's partial valences, speculation as to the structure of benzene by Claus and others reflected cracks in the adequacy of the classical representation of electron-pair bonds by solid lines. As structural methodology improved, some structures, especially of "electron-deficient" compounds, become sufficiently vague in bond terminology to be probably best defined by electron distributions and distances between nuclei. This approach is well refined in the chemistry of boranes and carboranes (1) but is not often applied to all-carbon electron-deficient systems. However, even the use of internuclear distances is not wholly satisfactory for defining structures of highly fluxional entities such as the $C_4H_7^+$ (2). The conundrum of the structure(s) of the $C_4H_7^+$ cation has been with us now for half a century (3–6) and has even been used in undergraduate chemical education to demonstrate the use of quantum-calculation software (7). Despite this, the experimental evidence directed to defining the structure of $C_4H_7^+$ is unconvincing to the extent that it is generally considered to be only consistent with the higher-level quantum calculations. That experiment takes a back seat here relative to theory is partly because $C_4H_7^+$ has a small number of atoms and electrons and can be regarded as well suited for the abilities of today's state of the *ab initio* art.

The best available calculations (2) suggest that in the gas phase there are three principal nearly equal-energy $C_4H_7^+$ structures, a cyclopropylcarbiny (cpc) structure, 1, and two bicyclobutonium (bc) structures, 2 and 3 (see Scheme 1). In the present study, the gas-phase calculations indicate 1 and 2 to be minima at the calculational level we used, and although 3 is of nearly the same energy as 2, it apparently does not represent an energy minimum.



Scheme 1. Structural formulas of $C_4H_7^+$ species.

Calculated geometries of 1 and 2 are shown in Fig. 1, in which the structures are represented primarily as three-dimensional geometric objects. The cpc structure 1 is more stable but only by 1.5 kcal/mol, and the energy barriers for conversion of the less-stable to more-stable structures are less than 1 kcal/mol. We find that small changes in the geometry of the symmetrical bc structure 3 can cause it to appear to be as little as 0.4 kcal/mol less stable than 2. Clearly, the potential-energy surface of $C_4H_7^+$ is nearly flat in the region connecting these three structures. Other calculations we have made include the allylcarbiny cation 4, the symmetrical cpc, and pyramidal structures (7, 8a, and 8b, respectively) as well as the β -methallyl cation 5.

Some distrust of theoretical calculations of $C_4H_7^+$ in the gaseous state is natural because at present little is known about

Abbreviations: cpc, cyclopropylcarbiny; bc, bicyclobutonium; ZPE, zero-point energies.

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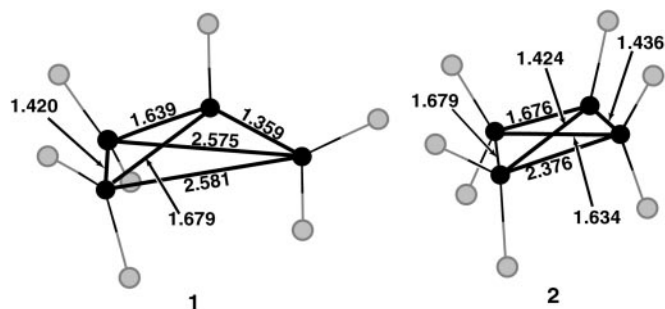


Fig. 1. Calculated geometries of structures 1 and 2.

$C_4H_7^+$ in the gas phase; but it is known that when the corresponding radical undergoes photoionization, the product quickly isomerizes to the β -methallyl cation **5** (8), a reaction not yet observed for $C_4H_7^+$ in solution. However, the energy of the $C_4H_7^+$ photoionization product may easily be sufficient to surmount the barrier that exists to the formation of **5**. More evidence for an exceptionally flat potential-energy surface, with a very small barrier to interconversion of $C_4H_7^+$ species, has been demonstrated recently in an experimental/theoretical gas-phase study by Crestoni and coworkers (9), who showed by ion-cyclotron resonance in the gas phase or in a microsolvated environment that the species present undergo structural equilibration within a time interval of $\leq 10^{-10}$ seconds, which in the Eyring formulation, with $\Delta\Delta S$ assumed to be zero, corresponds to a ≤ 4 kcal/mol activation energy at 270 K. Consequently, if the structures of $C_4H_7^+$ are to be defined by high-level calculations, the calculations should include solvents if they are to be relevant to the fascinating and complex chemistry of $C_4H_7^+$ in solution (6). We explore here how including solvents in a current level of quantum-mechanical calculations affects the energies, geometries, and electron distributions for the presumed fluxional isomers of $C_4H_7^+$.

Computational Procedures

The density functional theory approach we applied to the structures of $C_4H_7^+$ started with conventional structures in the gas phase and the JAGUAR program suite (Version 4.0, release 50) using B3LYP as the density functional theory functional and 6-31G** for the basis set. Zero-point energies (ZPE) were calculated by using a full Hessian evaluation. The calculations were repeated with simulations of cyclohexane, methanol, and water as solvent. JAGUAR utilizes a continuum dielectric solvent approach to calculate solvation energies in various solvents. The procedure involves constructing a solvent-accessible surface around the solute molecule. Inside this surface the dielectric constant is taken to be that of vacuum, whereas outside the surface the dielectric constant is taken to be that of the solvent. The electrostatic reaction field induced by the quantum-mechanical charge distribution of the solute is then represented by point charges on the solvent-accessible surface by solving the Poisson–Boltzmann equation. The solute wave function is solved iteratively in the presence of the reaction field to yield a new

quantum-mechanical charge distribution, and the charges representing the reaction field are recalculated by using the new charge distribution. The calculation is deemed converged when the reaction field and the quantum-mechanical charge distribution become self-consistent. Additionally, a “cavity” term is added to the energy to account for the energy required to create an opening in the solvent medium (10).

Results and Discussion

For comparison with earlier quantum-mechanical calculations, we calculated the total quantum-mechanical energies of the $C_4H_7^+$ system *in vacuo*. The results are shown in Table 1. Without solvent, the energy difference between structures 1 and 2 was 1.5 kcal/mol (2.1 kcal/mol with ZPE included), with structure 1 being the more stable. These results are slightly different from those reported by Saunders *et al.* (2) using MP4SDTQ/6-31G**//MP2(Full)/6-31G*, which indicated that the cpc structure 1 was less stable than the bcb structure 2 by 0.55 kcal/mol. The calculations of Koch *et al.* (11) are consistent with the latter findings. Concurrence of calculational methodology with experimental results in the $C_4H_7^+$ species can be drawn from a report by Aue (12), who has compared the experimental gas-phase values of ΔH_f° with values of ΔH_f° calculated at the CCSD(T)/ccpVTZ//MP2/6-31+G(d,p) level and found a difference of only 0.8 kcal/mol.

A fifth species, cpc cation 7 with its carbinyl carbon rotated such that its vacant *p*-orbital lies in a plane perpendicular to the plane of the cyclopropyl ring, has been discussed (2), but in our calculations using the same internuclear C—C dimensions as for 1, it failed to converge to a potential-energy minimum and had one imaginary vibrational frequency. Clearly, the results suggest that 7 is a transition state for rotation about the C1—C2 bond of 1.

The influence of solvent on the quantum-mechanical energy is seen most clearly from the solution-phase energies (13) listed in Table 1 and displayed in Fig. 2. The solution-phase energy is the total solute energy corrected for total solvent energy, solute cavity energy, a first-shell correction factor, and the ZPE correction. All four structures, 1, 2, 4, and 5, give comparable decreases in solution-phase energy in going from the gas to cyclohexane. As expected, all the cations are strongly stabilized in methanol and water, with the fluxional structure 2 being less stable in water than 1 by ≈ 0.3 kcal/mol. This result may not be significant as it appears, because energy differences of a few kcal/mol are likely to be within the uncertainty of the calculational methods, but we have no independent means of checking the accuracy of calculations for solvation of entities such as 1–3. The open-chain structure 4 is expected from the calculations to be more highly stabilized in polar solvents as the result of its rather localized positive charge. The conjugated open-chain 5, as expected, is correspondingly less stabilized in polar solvents because of delocalization of its positive charge.

The solvent-accessible surfaces of 1 and 2 are slightly different from one another, with 1 at 227 Å² and 2 at 216 Å², and this difference should contribute to the greater calculated solvent stabilization of the bcb species 2. Unexpected and noteworthy is the calculated greater efficacy of methanol over water in stabi-

Table 1. Solution-phase energies with ZPE in kcal/mol of 1, 2, 4, and 5 cation species calculated for vacuum and three solvents relative to 5 in methanol

Structure	Cation	Vacuum	Cyclohexane	Methanol	Water
1	Cyclopropylcarbinyl	74.54	42.13	12.79	13.40
2	Bicyclobutonium	76.65	43.54	13.16	13.70
4	Allylcarbinyl	94.89	61.31	28.72	30.05
5	Methylallyl	60.76	28.46	0.00	2.23

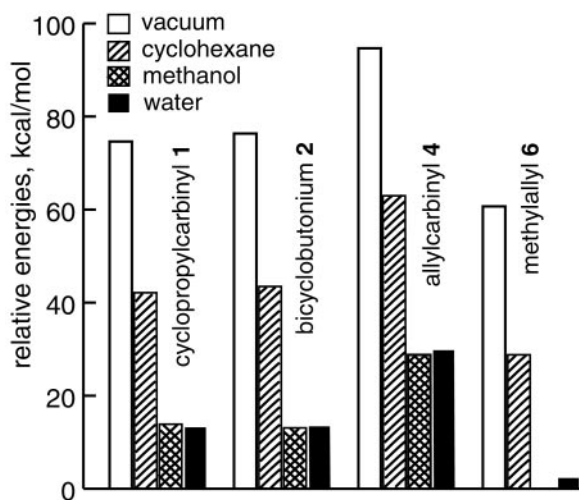


Fig. 2. Solution-phase energies with ZPE of solvated and unsolvated $C_4H_7^+$ cations relative to that of 5 in methanol.

lizing the cations. This may be partly the result of a greater cost in energy for making a solvent cavity to accommodate the hydrocarbon cation in water than in methanol.

Finally, one can examine the solvation energy (solution-phase energy minus gas-phase energy). The results of these calculations are assembled in Table 2. For a given solvent, the same relative effects are seen as for solution-phase energy calculations. The cpc structure is less stabilized in all solvents than is the bcb structure. Hence, the relative stability of these two species is suggested here to reverse in polar solvents. The total calculated stabilization of 4 is now substantially greater in polar solvents than that of 5 (see Fig. 3). For the solvation-energy calculations, methanol is similar to water in stabilizing the cation. This is expected here because of the interrelation of solution-phase energy and solvation energy. With 1 and 2, the degree of stabilization by solvent accords with the dielectric constants, but with 4 and 5, methanol seems more effective than water.

Calculations of ΔG at 0 and 298.15 K indicate that the free energy is insensitive to temperature changes in the gas phase, cyclohexane and methanol. On the other hand, the computed ΔG value of 0.3 kcal/mol at 0 K for the energy difference between 1 and 2 in water increases to 1.7 kcal/mol at 298.15 K.

Low-temperature ^{13}C spectra of $C_4H_7^+$ generated in superacid from either cyclopropylcarbiniol or cyclobutanol are the same and consistent with rapidly equilibrating CH_2 groups. However, the average chemical shift changes substantially with temperature (14), which indicates energy differences between the species present. Low-temperature vibrational spectra observed for $C_4H_7^+$ formed from C_4H_7Cl isomers in an antimony pentafluoride

Table 2. Calculated solvation energies in kcal/mol of 1, 2, 4, and 5 cationic species for three solvents

Structure	Cation	Cyclohexane	Methanol	Water
1	Cyclopropylcarbiniyl	−32.41 (−34.21)	−61.72 (−61.74)	−59.34 (−60.92)
2	Bicyclobutonium	−32.95 (−33.09)	−63.43 (−63.47)	−62.62 (−62.93)
4	Allylcarbiniyl	−33.81 (−33.59)	−66.19 (−66.18)	−64.91 (−64.84)
5	Methylallyl	−31.90 (−32.30)	−60.70 (−60.76)	−58.38 (−58.53)

Parentetical values include ZPE.

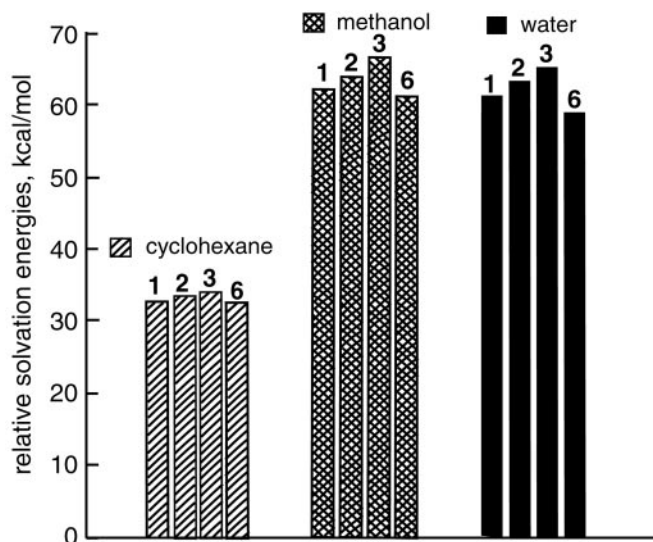


Fig. 3. Calculated solvation energies of $C_4H_7^+$ cations including ZPE corrections.

ride matrix are reported to be consistent with a mixture of cpc and bcb isomers (15). The $^{13}CPMAS$ (cross-polarization with magic-angle spinning) spectra of $C_4H_7^+$ from ^{13}C -labeled cpc chloride in antimony pentafluoride at low temperatures indicate fast equilibration at 170 K, which slows, perhaps not surprisingly, at 100 K (16). All these observations are reflective of a quite flat potential-energy surface containing 1 and 2 with a low energy barrier for interconversion of 1 and 2.

There is a small systematic change in the geometry of the most highly delocalized structures 1 and 2 going from the gas to water or methanol. The internuclear distances contract approximately uniformly <0.002 Å for structures 1 and 2 except for the longest and most electron-deficient C—C bond of 2, which contracts by 0.005 Å. These small bond-length changes with solvent polarity are also calculated for the open-chain structures, with a larger decrease (0.008 Å) for the C—C bond nearest the localized charge for 4 and by 0.004 Å for the allylic C—C bonds of 5. Aue (17) suggests that structure and properties calculated for the gas phase are not likely to be seriously perturbed by solvation. Hehre *et al.* (18), recognizing the importance of solvation on S_N2

Table 3. Comparison of edge lengths for structures 1 and 2

Bond numbers	1	2	Absolute difference
1,2	1.359	1.436	0.077
2,3	1.679	1.424	0.255
2,4	1.639	1.676	0.037
1,3	2.581	2.376	0.205
1,4	2.575	1.643	0.932
3,4	1.420	1.679	0.259

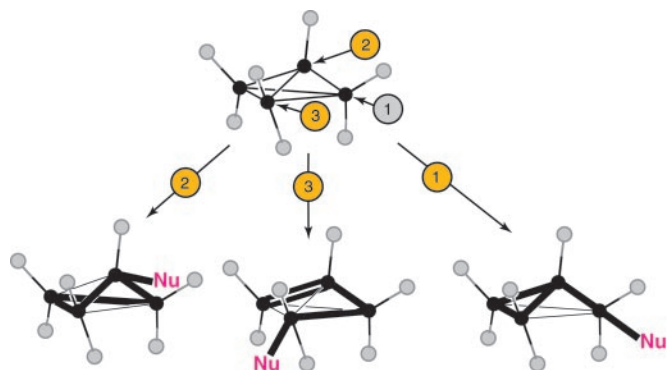


Fig. 4. Product-forming scheme for $C_4H_7^+$ from minimum-energy bridged structure. Attack of a nucleophile at positions 1, 2, and 3 leads to the products shown.

reactions, believe that inclusion of polar solvent effects could suggest actual changes in reaction mechanism.

The geometries of **1** and **2** are calculated to undergo only small changes through their interconversion as shown in Table 3, where only the C3—C4 bond experiences a significant change of length. This is associated almost entirely with an arcing motion of C4 in the basal plane formed of C2—C4. The similarity of geometries of the cations that yield the products formed in the reactions of $C_4H_7^+$ is better represented geometrically with lines along the edges of polyhedra rather than by electron-pair bonds (Fig. 4).

With **1** and **2**, attack of a nucleophile may occur at positions 1, 2, or 3 of Fig. 4 on a single face and produce the observed cpc, cyclobutyl, and allylcarbinyl products, respectively. Under conditions of kinetic control, the cpc and cyclobutyl products are usually formed in comparable amounts and the allylcarbinyl product to the extent of only a few percent. When thermodynamic control dominates, more cyclobutyl product is formed first, which then leads to essentially exclusive allylcarbinyl product. Our electrostatic potential calculations shown in Fig. 5 and Mulliken population calculations (19, 20) indicate the lowest electron density (blue) at position 1 in the cpc structure, at position 2 in the ccb structure, and relatively higher electron densities (red represents the highest) at position 3 for both structures, which is in general agreement with the experimental product distributions. The electrostatic potential converges with increasing size of basis sets, whereas the Mulliken analysis does not. Nonetheless, the Mulliken populations parallel the electrostatic potential surfaces (21, 22). Molecular electrostatics have become an important way to visualize electron density on the surface of a molecule. Electrostatic potential maps at 0.05

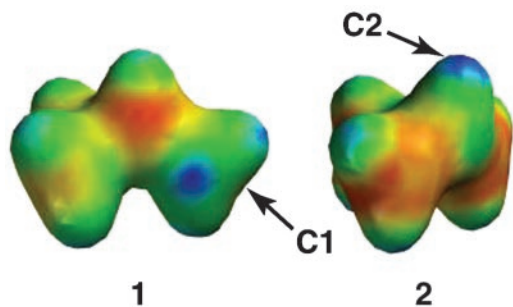


Fig. 5. Electrostatic potential surface of **1** and **2** at a potential density of $0.05 \text{ e}^- \text{ per a.u.}^3$, where blue represents the minimum electron density.

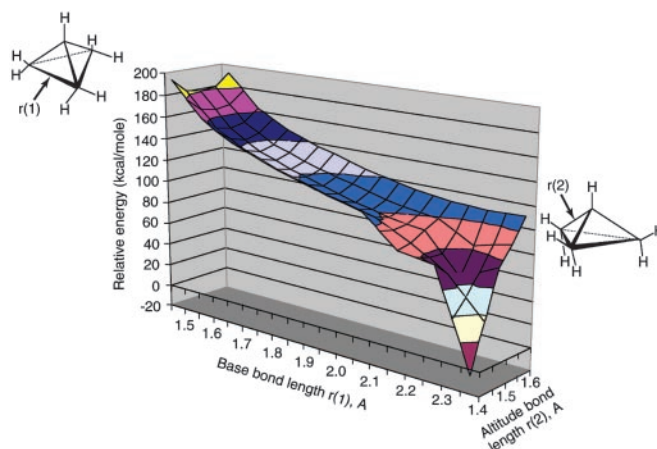


Fig. 6. Energy as a function of geometry for the C_{3v} cation.

$\text{e}^-/\text{a.u.}^3$ show clear minimum electron densities at C1 of **1** and C2 of **2** (Fig. 5).

A possible role for the tricyclobutonium ion with three equivalent CH_2 groups, displaying C_{3v} symmetry, was postulated in 1951 to account for observed extensive shuffling of isotopic carbon labels and an indication of possible stabilization as a three-centered system with two electrons, analogous to H_3^+ (4). A later investigation (23) of the tricyclobutonium structure by the Hückel linear combination of atomic orbital (LCAO) theory showed the importance of the rotational orientation of the CH_2 groups. The orientation with the methylenes turned to bring all their hydrogen atoms into the same (basal) plane of the carbon skeleton (**8a**) is more favorable in the LCAO treatment than is the structure with the methylene hydrogens oriented with three hydrogens in a plane above and three below the basal plane (**8b**).

We have calculated a potential-energy surface for the symmetrical C_{3v} structure as a function of the length of its edges (Fig. 6), which gives different results. Here, r_1 is taken as the distance between CH and CH_2 along the 1.5-Å edges, and r_2 is taken as the distance between CH_2 and CH_2 . Now, when r_1 is changed over a reasonable range of values and r_2 is allowed to systematically increase, the potential-energy surface appears as a descending trough, with the optimum value for r_1 near 1.5 Å. In the very high-energy region, the structure is **8a**, but at r_2 of ≈ 2.2 Å, the structure spontaneously shifts over to **8b**. Then, when the constraint on C_{3v} symmetry is relaxed, the C_2 structure follows an energetically steep descent of ≈ 100 kcal/mol to **1**.

In summary, the elusive structure of the $C_4H_7^+$ system, even after a half a century of continuing controversy, still presents an interesting structural problem. To be sure, theoretical calculations seem to be narrowing the range of possible geometrical arrangements, but new experiments are needed to investigate and confirm the theoretical calculations for this ion both in the gas phase and in solution, where the calculations indicate that the differential solvent effects should be relatively small even when the solvation-energy differences from one solvent to another are large. However, although the calculated differential solvent effects are small in an absolute sense, they are still large compared with the energy differences between **1** and **2**.

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